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Valorization of underutilized river tamarind *Leucaena leucocephala* seeds biomass for cellulose nanocrystals synthesis

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ABSTRACT

River tamarind or scientifically *Leucaena leucocephala,* is one of the underutilized nanocellulose resources with the potential to be used in reinforcement materials. This work evaluated the use of the insoluble residual waste or marc obtained during the isolation of galactomannan from *Leucaena leucocephala* seed (LLS) as a feedstock of cellulose to obtain cellulose nanocrystals by a two-step acid hydrolysis followed by its characterization and morphological study. The first step involved acid hydrolyzation of the hemicellulose and lignin from LLS, while the second step dealt with the removal of the amorphous region to produce crystalline LLS nanocrystals (NLLS). The physicochemical properties of nanocrystals were characterized using the Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), particle size analyzer (PSA), X-ray diffractometer (XRD), thermal gravimetric analysis (TGA), and gel permeation chromatography (GPC). The NLLS isolated showed a rod-like structure in the range of 70–90nm in diameter with a crystallinity index of 76% and thermal stability at 264°C. PSA indicates that 97.5% of the size distribution of NLLS was below 136.9nm. GPC analysis also revealed that the sulphuric acid hydrolyzation during the second step caused a reduction in the molecular weight due to the cleaving of glycosidic bonds in the structure. These results indicated that LLS waste is a potential feedstock for cellulose nanocrystals preparation.

1. Introduction

Nanocellulose is a nano-sized cellulosic material that has been widely studied in numerous fields, including in the pharmaceutical, textile, and biomaterial industries due to its interesting physical and chemical properties (Othman, 2014; Lin and Dufresne, 2014; Ilham and Nimme, 2019). For instance, nanocellulose is known to be biodegradable, biocompatible, has a high specific modulus and stability in most solvents, and low cytotoxicity. These allow it to be utilized as a polymer matrix, electrical materials for energy storage, and drug delivery (Jorfi and Foster, 2015; Chen and Hu, 2018). Nanocellulose is derived from the crystalline and amorphous regions of cellulose through various methods. Depending on the type of the lignocellulosic materials used, and the methods employed, the physicochemical properties of the nanocellulose can be altered (Khalil et al., 2014). These include the types of acid used for hydrolysis and the preparation techniques. There are two types of nanocellulose, which are cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF).

Cellulose nanocrystals (CNC) are rod-like or needle-like cellulose crystals, ranging from the 5-70nm diameter and 100-250nm in length. They are produced from the hydrolyzation with strong acid to remove the non-cellulosic components and most amorphous cellulose, which resulted in a near-perfect crystallinity (Abitbol et al., 2016). On the contrary, cellulose nanofibrils (CNF) are long and entangled fibrils, have a high aspect ratio, and flexible (Abitbol et al., 2016). They appear as a highly viscous suspension at low concentration due to the clumping of the long fibers. They are generated through the exertion of high pressure before and/or

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after chemical or enzymatic treatment on the cellulose.

Different types of acids used in producing nanocellulose will influence the properties of the nanocellulose formed. For example, nanocellulose produced from sulphuric acid shows poor thermostability due to the presence of sulfate groups, which results in a negatively charged surface. Nonetheless, the colloidal suspension of the sulphuric acid-treated nanocellulose is more stable compared to those prepared with hydrochloric acid (Bano and Negi, 2017; Fahma et al., 2010).

In recent years, there has been a significant interest in the extraction of cellulose nanocrystals from various sources. Nanocellulose isolation normally involves three important steps: (1) extraction with an organic solvent removal of fats, oils, resins, and waxes, (2) bleaching for delignification, and (3) treatment with a strong alkaline solution to remove hemicellulose. Many pretreatment processes have been reported for cellulose isolation, such as pulping, grinding, and acid hydrolysis (Abitbol et al., 2016).

Pretreatment methods are employed to disrupt the structure to aid in the removal of lignin, hemicellulose, and other lignocellulosic materials. Bleaching and alkali treatment help in isolating cellulose nanocrystals. (Rabemanolontsoa and Saka, 2016; Kim et al., 2016). However, this method is associated with a low yield of cellulose, time-consuming, and involves repetitive bleaching. Bleaching uses sodium chloride, which produces toxic chlorinated compounds as by-products and is harmful to the environment (Karimi and Taherzadeh, 2016).

This study aimed to extract cellulose nanocrystals from the insoluble residual waste or marc obtained during the isolation of galactomannan from mature seeds of *Leucaena leucocephala* (LLS). In Malaysia, LLS is commonly known as Petai Belalang. Other names include river tamarind, lead tree, white lead-tree, white popinac, wild tamarind, kubabul, subabul, ipil ipil, kariskis, palo-maria faux mimosa, kladingan, lamtoro, tagarai krathin, and tobao. It can be found abundant throughout Malaysia and is underutilized, making it a sustainable source.

A two-step acid hydrolysis process was employed in extracting the cellulose nanocrystals from LLS. A mixture of acetic acid and nitric acid was used to aid in the fragmentation of hemicellulose and lignin in LLS. This saves time and reduces the amount of cellulose lost to the process. Next, LLS was treated with sulphuric acid to extract the cellulose nanocrystals. To date, no research has been reported on the preparation of cellulose nanocrystals from LLS by using these methods. The properties and characteristics of the cellulose nanocrystals were evaluated using the FTIR, FESEM, TEM, XRD, PSA, GPC, and TGA. Since cellulose nanocrystals have distinct properties, optimizing LLS cellulose nanocrystals to be used in industrial applications can be beneficial.

2. Experimental and methods

2.1. Cellulose and nano cellulose preparation

Chemical compositions (cellulose, hemicelluloses, and lignin) were determined according to the methods reported by the Technical Association of Pulp and Paper Industry (TAPPI) (Brendel et al., 2000). The insoluble residual waste or marc of LLS was obtained based on Rahim et al. (2018). The extraction of LLS cellulose was adopted from Husin et al. (2017). Briefly, the dried LLS was treated with a mixture of 80% of acetic acid and 65% of the nitric acid solution for 1 hour at 90°C.

The cellulose nanocrystals were prepared as described by Jiang and Hsieh (2015). 10g of cellulose was hydrolyzed in 64% H_2SO_4 (96% purity) solution with an acid (fiber/acid ratio of 1:10) at 50°C under vigorous agitation for 60min. One liter of cold water was added to the reaction mixture to form cellulose nanocrystals suspension. The suspension was then rotated at 10,000 rpm for 10min to form precipitation. The process was repeated until the suspension reached pH 6. Next, dialysis was performed (3,000 Molecular Weight Cut Off) until the pH reached neutral.

2.2. Characterization

The soluble cellulose and cellulose nanocrystals were prepared based on Han et al. (2008) with slight modifications. Two solutions were prepared; (A) 6g of dried LLS cellulose nanocrystals dissolved in 100ml of Me_2SO containing 48g of urea (8 M) and (B) 100ml of Me_2SO mixed with 10ml of concentrated H_2SO_4 heated in a water bath at 100°C. Next, solution A was added dropwise to solution B for 6 hours with stirring to form cellulose sulfate nanocrystals solution.

The solution was then diluted in 2 liters of deionized water and dialyzed for 5 days to remove any unreacted microparticulate cellulose. The cellulose sulfate nanocrystals extracted were collected and dried at room temperature. A scanning electron microscope (JEOL JSM-7600F) was used to observe the morphology of the LLS nanocrystals. The nanocrystals were mounted on aluminum stubs with carbon tapes, and the accelerating voltage was set at 10kV. A transmission electron microscope (LIBRA 120, Germany) with an acceleration voltage of 120kV was used to determine the dimensions of the nanocrystals. A drop of a diluted suspension of the cellulose nanocrystals (1wt.%) was deposited on the surface of a carbon-coated Cu grid. The dimensions of the cellulose nanocrystals were determined using digital image analyses (Image J). Around 30-50 individual nanocrystals were randomly selected to determine its average length and diameter, respectively.

The identification of the chemical properties of the nanocrystals was made by using the Fourier transform infrared spectroscopy (FTIR). Ultrathin pellets were prepared by mixing 2mg of nanocrystals

with potassium bromide, KBr powder and were tested in the range of 450-4500cm^{-1} to obtain their IR spectra (Perkin-Elmer Spectrum 100IR spectrophotometer). A Netzsch thermogravimetric analyzer (TG209 F3 Tarsus model) was used to study the thermal behavior of the nanocrystals. 10.0±1.0mg of nanocrystals was subjected to varying temperatures ranging from 30–600°C at a rate of 10°C/min under a nitrogenic atmosphere with a gas flow of 80cm^3/min. Particle size was measured by dynamic light scattering (DLS, Zetasizer Nano S90, and Malvern).

The crystallinity of the nanocrystals was analyzed by using an X-ray diffractometer (X'Pert PRO MD PANalytical) with CuKα radiation at 35kV and 30mA. The crystallinity index was calculated as described by Segal et al. (1959). The molecular weights of the cellulose and cellulose nanocrystals were determined by gel permeation chromatography (GPC). A standard calibration curve was prepared by dissolving 2mg of dextran in 2ml of distilled water. The molecular weights of the cellulose and cellulose nanocrystals were determined from the dextran standard calibration curve (molecular weight of dextran standards versus elution time).

3. Results and discussion

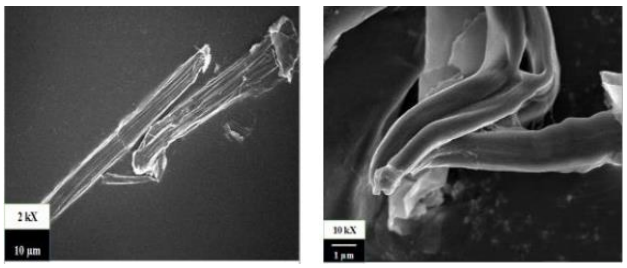
3.1. Hemicellulose and cellulose contents

The LLS contained 37.4±1.8 of cellulose, 30.6±1.5% of hemicellulose, and 16.1±2.3% of lignin. LLS cellulose nanocrystals yield was low at 27%, probably owing to the excessive degradation following sulphuric acid treatment. Xie et al. (2018) reported on the lower cellulose nanocrystals yield (<30%) isolated through sulphuric acid hydrolysis (Xie et al., 2018). However, Chen et al. (2016) stated that decreasing the concentration of sulphuric acid and prolonging the reaction could help increase the yield of cellulose nanocrystals. LLS has a higher cellulose content compared to the melon seed shell (16.5%) but lower than the mango seed (55%) (Lu et al., 2016; Pius et al., 2014).

3.2. Morphological structure of cellulose nanocrystals

FESEM micrographs in Fig. 1 show the structure of the cellulose nanocrystals after the sulphuric acid hydrolyzation. The cellulose nanocrystals were negatively stained due to the conjugation of sulphuric acid moieties during the hydrolyzation. It can be observed that the nanocrystals are rod-like in shape, smaller in size and diameter (Fig. 1a), and tend to be in a cluster formation (Fig. 1b).

TEM images for the LLS cellulose nanocrystals (Fig. 2) observed individual long fibers with diameter ranges from 2–11nm. Since it is hard to discern the ends of the fibers in the bundles, an accurate estimation of their length could not be determined. It was estimated that the length of the fibers is 200nm–300nm in length. The nanocellulose fibers were seen to be laterally aggregated in clumps that formed a network due to a high specific area and strong hydrogen bonds interactions between the fibers (Henrique et al., 2013). Similar arrangements have been shown in the Isora nanofibrils and nanocrystals of mango seed, tomato peel, and banana peel (Chirayil et al., 2014; Pius et al., 2014; Jiang and Hsieh, 2015).



(a) (b)

Fig. 1: Scanning electron micrograph (a) individual particle of cellulose nanocrystals (b) agglomeration of cellulose nanocrystals

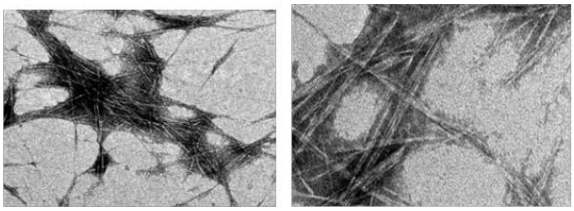


Fig. 2: Transmission electron micrograph of LLS (cellulose nanocrystals)

The aspect ratio of the nanocrystals was calculated to be between 70–90, which is considerably high. Cellulose nanocrystals with a high aspect ratio typically have high reinforcement ability (George and Sabapathi, 2015). This makes LLS nanocrystals suitable to be used as a reinforcement material in biocomposites in improving their mechanical strength. NLLS cellulose nanocrystals clusters were found to be distributed in two sizes (Fig. 3). 97.5% of the particles were 136.9nm, and 2.5% were about 4302nm. Tibolla et al. (2017) saw similar observations in the acid hydrolysis isolation of cellulose nanoparticles from other sources. However, the particle size distributions of the LLS nanocrystals are different from the TEM results. Nanocellulose has a long rod-like shape, and its diameter varies from 10nm to 80nm, whereby its length ranges from 100nm to 1000nm (Henrique et al., 2013; Pius et al., 2014).

3.3. FTIR spectra of cellulose nanocrystals

Fig. 4 illustrates the FTIR spectra of nanocellulose-LLS (NLLS) and cellulose-LLS (CLLS). From Fig. 4, it can be seen that CLLS has two absorption peaks at 1730cm^{-1} and 1551cm^{-1}. This is due to the C=O and C=C stretching in the acetyl and uronic ester groups of lignin and/or hemicellulose (Mendes et al., 2015). No absorption was found in NLLS in these regions, indicating the absence of hemicellulose and lignin in the structure. However,

NLSS showed absorbance at 1203cm^{-1}, owing to the vibration of the S=O sulphuric acid moieties on the surface of the structure (Jonoobi et al., 2011).

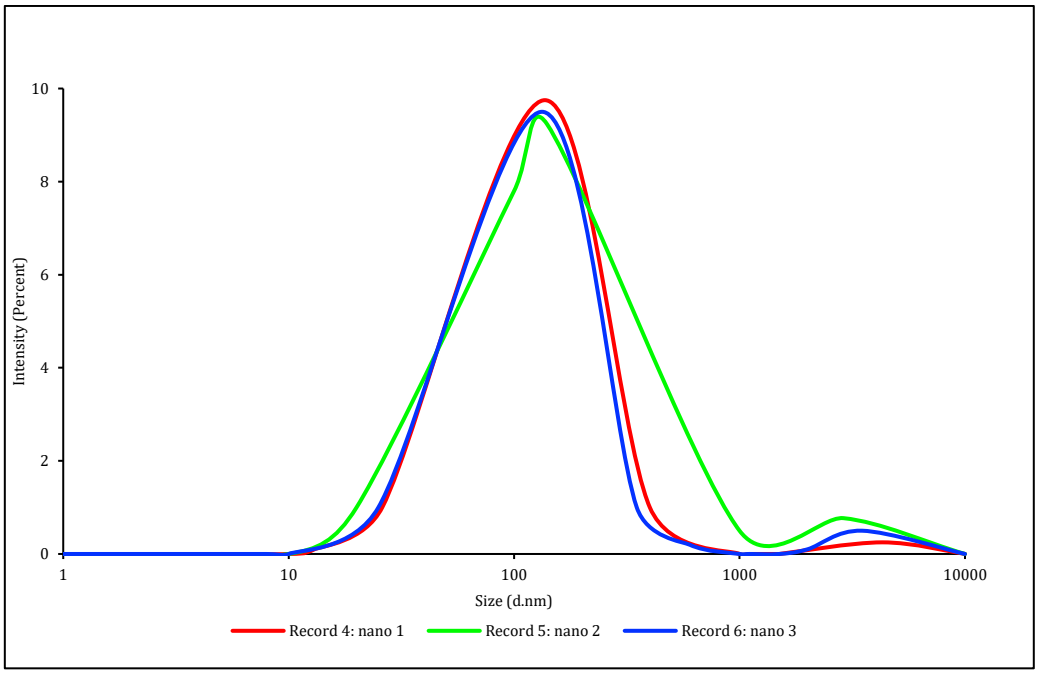


Fig. 3: Particle size distribution of cellulose nanocrystals

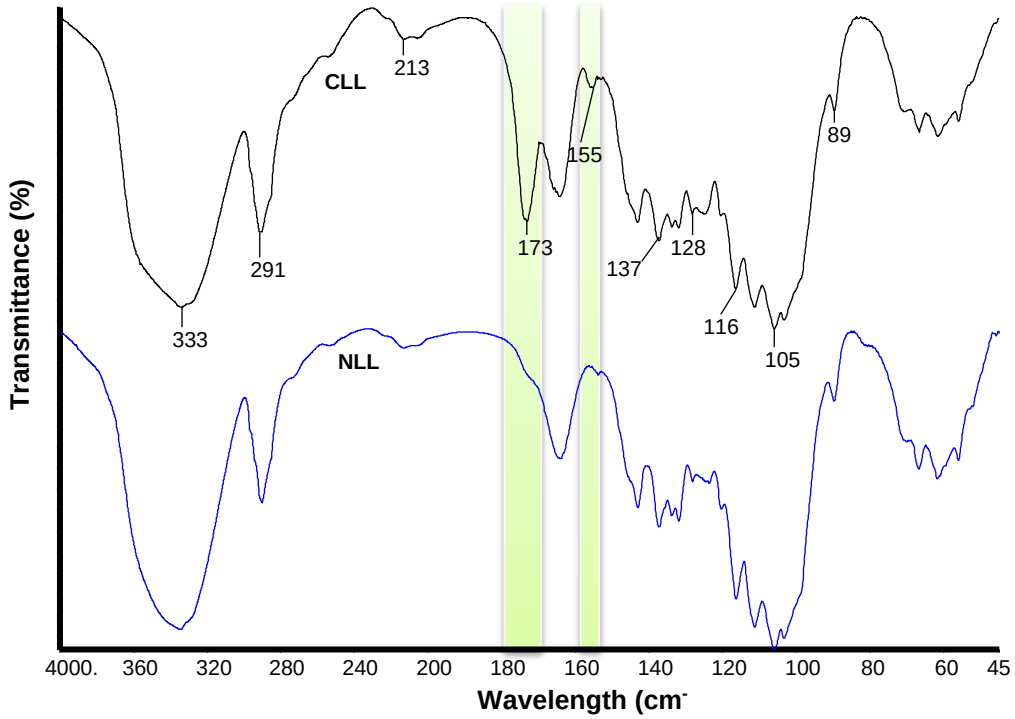


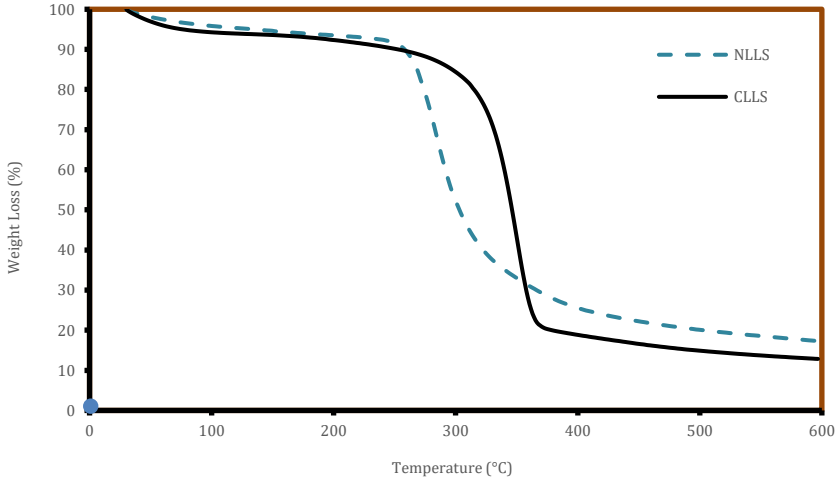
Fig. 4: FTIR spectra of NLLS in comparison with CLLS

3.4. Thermal behavior

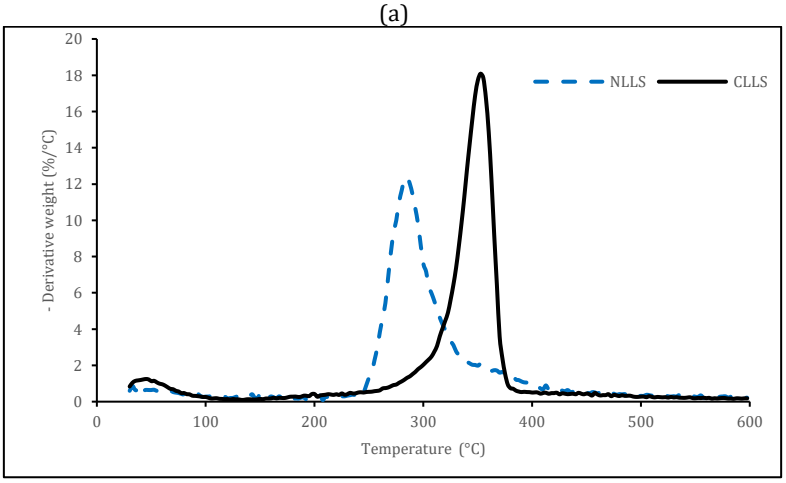
The properties of NLLS and CLLS under thermal decomposition were shown in Fig. 5. Thermal decomposition of both celluloses involves the vaporization and removal of bound water from the structure. In both structures, a small weight loss was observed at 30°C–100°C, which can be attributed to the removal of residual water from the celluloses. At 320.8°C, CLLS was found to have the highest weight loss indicating maximum decomposition. In contrast, NLLS was seen to decompose at a lower temperature at 273.6°C due to the presence of sulfate group moieties on the surface of the structure. Smyth et al. (2017) stated that the thermostability of cellulose nanocrystals tend to decrease with higher sulfate groups content. Hence, NLLS needed less activation energy is to breakdown its structure (Morais et al., 2013). Jiang and Hsieh (2015) reported a similar finding on the isolation of nanocellulose from tomato peels. At 600°C, NLLS (17.26wt%) was observed to retain more weight compared to CLLS (12.80wt%). This might be attributed to the higher crystallinity of

NLLS, which made it flame resistant at high temperatures (Chirayil et al., 2014).

García et al. (2016) indicated that high crystallinities are associated with high thermal degradation. Mandal and Chakrabarty (2011) showed nanocomposites consisted of nanocellulose composites (NCC) have better resistance towards thermal degradation. The addition of NCC reinforces the interaction in the matrix through hydrogen bonding, which increases the thermal energy needed to break the bonds (Mandal and Chakrabarty, 2011). Consequently, this improves the thermal stability of the NCC.



(a)



(b)

Fig. 5: Comparison of (a) TG and (b) DTG curves of cellulose and cellulose nanocrystals

3.5. Crystallinity index of the cellulose nanocrystals

The diffractograms for CLLS and NLLS (Fig. 6) showed that both celluloses peaked at 2θ=18.2° and 22.6°, respectively. These peaks are common for cellulose type 1. Sèbe et al. (2012) showed the typical peaks for cellulose were at 15.7° and 22.6°. The crystallinity index of CLLS (57.5%) was found to be lower than that of NLLS (75.9%). Higher crystallinity index in NLLS indicates that the treatment of sulphuric acid was able to remove the residual hemicellulose and lignin in the cellulose structure, leaving only the crystalline parts intact. High crystallinity nanocrystals are more firm and rigid, which makes it suitable to be used as nanocomposites in reinforcement materials. Marett et al. (2017) reported that an additional 5wt% of CNCs isolated from pistachio shells in a TPU composite increased its modulus elasticity, providing higher yield stress in the composite.

LLS cellulose nanocrystals were also shown to have a higher crystallinity index compared to the nanocrystals isolated from pomelo waste (60.3%), sweet potato residue (72.5%), and coconut husk (65.9%) (García et al., 2016). Haafiz et al. (2014) and Chirayil et al. (2014) observed a higher crystallinity index in nanocrystals isolated from oil palm biomass (88%) and isora fiber (90%). Nevertheless, the crystallinity index of nanocrystals is highly dependent on the techniques employed throughout the extraction process. Cherian et al. (2008) and Husin et al. (2019) saw a range of crystallinities (74%-91%) for the nanocrystals isolated from banana fibers and medicinal cotton by changing the pretreatments for cellulose pulping. Li et al. (2009) stated that the parallel rearrangement and growth of the monocrystals of the cellulose nanocrystals during the preparation might improve its

crystallinity. Details on the crystallinity index and thermal stability of various nanocellulose resources are depicted in Table 1.

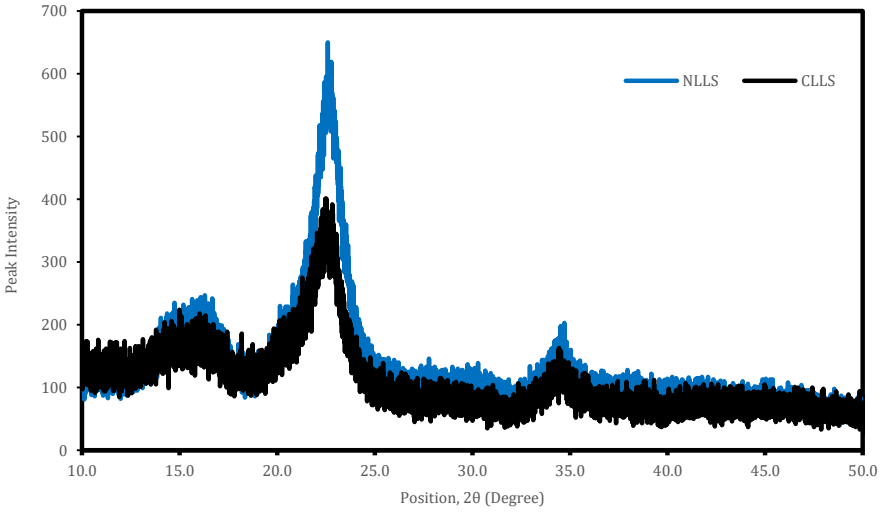


Fig. 6: XRD patterns of (a) cellulose (CLLS) and (b) cellulose nanocrystals (NLLS)

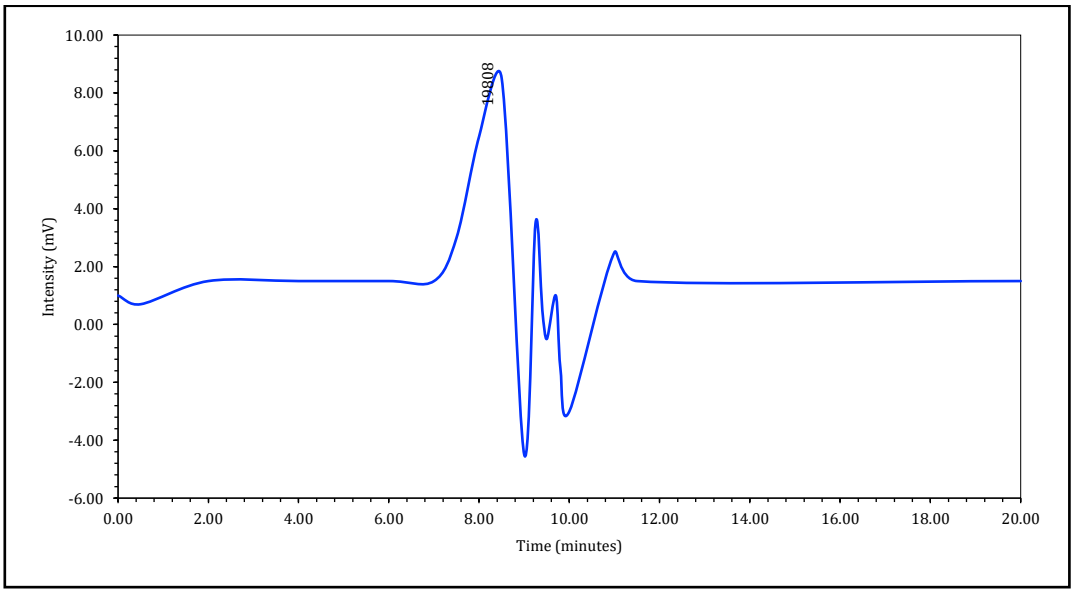
Table 1: Crytallinity index and thermal stability of various nanocellulose resources

	Nanocellulose Resources	Crystallinity Index (%)	Thermal Stability (°C)	References
1	River Tamarind Seeds	76	264	This study
2	Pomelo Waste	60.3	235	García et al. (2016)
3	Oil Palm Biomass	88	273	Haafiz et al. (2014)
4	Isora Fibre	90	284	Chirayil et al. (2014)
5	Sweet Potato Residue	72.5	258	García et al. (2016)
6	Coconut Husk	65.9	241	García et al. (2016)
7	Banana Fibre	74	255	Cherian et al. (2008)

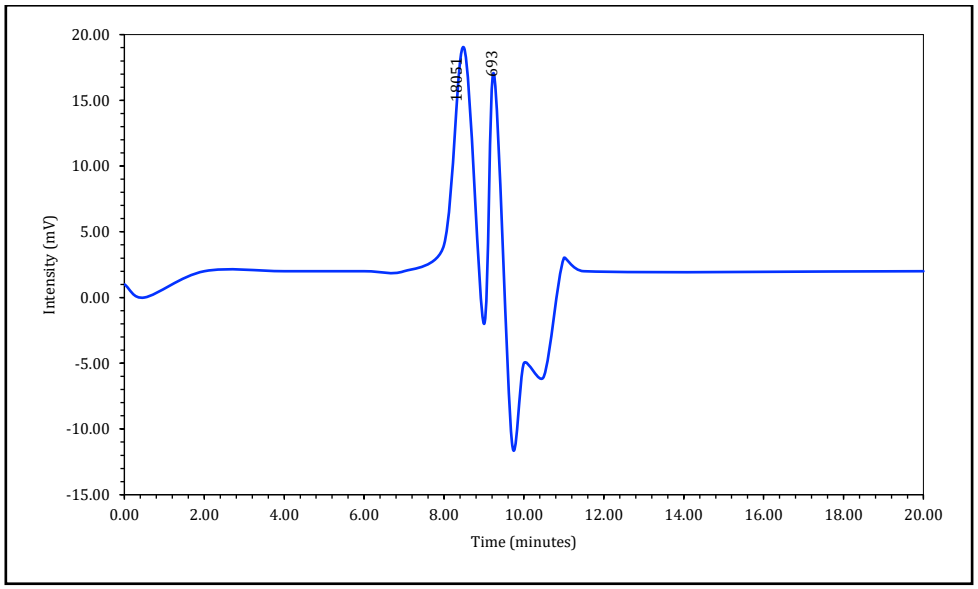
3.6. The molecular weight of the cellulose nanocrystals

Fig. 7 depicts the GPC chromatogram of CLLS and NLLS. Both celluloses peaked at 8.5 mins, which correlates with the retention time of cellulose (9.2 mins) observed by Haafiz et al. (2014).

CLLS (14kDa) was found to have a lower molecular weight compared to NLLS (11kDa). Hydrolysation of the CLLS with sulphuric acid caused the cleaving of the glycosidic bonds to remove the hemicellulose and lignin. This resulted in a lower molecular weight in NLSS as only the crystalline molecules remained in the structure.



(a)



(b)

Fig. 7: GPC of (a) cellulose and (b) cellulose nanocrystals

4. Conclusion

Cellulose nanocrystals have been known to have various potentials to be used in industries. They are commonly derived from abundant and underutilized sources, cheap, biocompatible and biodegradable. These make them attractive sources to be employed as nanocomposites. Insoluble waste from the mature seeds of *Leucaena leucocephala* (LLS) is one of the underutilized nanocellulose sources with the potential to be optimized as nanocomposites. In this study, a preliminary synthesis method for producing cellulose nanocrystals for use on an industrial scale has been explored. However, in future work, optimization of the parameters, including acid concentration, should be studied.

It was successfully shown that a two-step acid hydrolysis extraction of LLS is able to produce cellulose nanocrystals. The two-step acid hydrolysis is able to reduce the amount of cellulose degraded throughout the process. LLS yielded 27% of cellulose nanocrystals with the thermal stability of 273.6°C and a crystallinity index of 75.9%. FTIR analysis confirmed that most hemicellulose and lignin were removed during the acid hydrolysis. GPC analysis showed that the molecular weight of cellulose decreased after sulphuric acid hydrolyzation due to the breaking down of hemicellulose and lignin in the structure of the cellulose. The results from this study showed the possible use of the insoluble residual waste or marc obtained during the isolation of galactomannan from *Leucaena leucocephala* seed (LLS) could be a feedstock for nanocellulose production by a two-step acid hydrolysis process.

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Compliance with ethical standards

Conflict of interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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